

P15442SG-ALM/jw

DESCRIPTION OF INVENTION

"IMPROVEMENTS IN OR RELATING TO SOLDERS"

THIS INVENTION relates to solders, and in particular, to solders which are substantially lead-free.

Many conventional solders contain lead as a major constituent thereof. Such solders often have desirable physical properties, and the use of lead-containing solders is widespread throughout several industries, including those concerned with the production of printed circuit boards. For example, a solder containing a 63% tin and 37% lead is commonly used in wave-soldering processes.

However, there are increasing demands for lead-free solders, due, for example, to environmental considerations, and it seems likely that, within the next few years, it will be a legal requirement in several countries for solders used in the manufacture of many items to contain little or no lead.

Previous attempts to formulate lead-free solders have met with limited success. Conventional lead-free solders generally have undesirable physical properties, including poor wetting properties, low fluidity, poor compatibility with existing component coatings and excessive drossing. A particular problem

which has been recognised in the use of lead-free solders is the issue of fillet lifting, where a fillet of solder at the edge of a through-plated hole in a printed circuit board tends to separate from the underlying material, for example, a nickel/gold coating. Another problem is the fact that lead-free solders tend to have a high dissolution rate for copper, so that copper is leached into the lead-free solder from components and circuit boards in contact with the solder.

As a result, some manufacturers are finding that existing soldering processes which have functioned effectively for many years must now be significantly adapted to accommodate the use of lead-free solders. In addition, the existing materials that are employed in the production of printed circuit boards may have to be replaced in order to be compatible with the use of lead-free solders. This adaptation of processes and materials is widely regarded as a poor use of resources, particularly as the standard of articles manufactured using known lead-free solders is, as indicated above, often considerably below that achievable using conventional leaded solders.

It is an object of the present invention to provide a lead-free solder which is able to serve as a more or less direct substitute for conventional lead-containing solders.

Accordingly, in one aspect of the present invention, there is provided a substantially lead-free solder comprising: from 88.5% to 93.2% tin; from 3.5% to 4.5% silver; from 2.0% to 6.0% indium; and from 0.3% to 1.0% copper.

A solder embodying the invention may also comprise up 0.5% of an anti-oxidant or anti-skinning additive, such as phosphorous or another non-metallic compound or element.

In a preferred embodiment, the solder comprises 91.3% tin, 4.2% silver, 4.0% indium and 0.5% copper.

In another preferred embodiment, the solder comprises 91.39% tin, 4.1% silver, 4.0% indium, 0.5% copper and 0.01% phosphorous.

In another aspect of the present invention, there is provided a method of preparing a substantially lead-free solder, comprising the step of mixing tin, silver, indium and copper such that: the proportion of tin in the solder is from 88.5% to 93.2%; the proportion of silver in the solder is from 3.5% to 4.5%; the proportion of indium in the solder is from 2.0% to 6.0%; and the proportion of copper in the solder is from 0.3% to 1.0%.

A method of preparing a solder in accordance with the invention may comprise including up to 0.5% of an anti-oxidant or anti-skinning additive in the solder mixture.

A preferred method of preparing a solder in accordance with the invention comprises the step of mixing tin, silver, indium and copper such that: the proportion of tin in the solder is 91.3%; the proportion of silver in the solder is 4.2%; the proportion of indium in the solder is 4.0%; and the proportion of copper in the solder is 0.5%.

Another preferred method of preparing a solder in accordance with the invention comprises the step of mixing tin, silver, indium, copper and phosphorous such that: the proportion of tin in the solder is 91.39%; the proportion of silver in the solder is 4.1%; the proportion of indium in the

104789-0022560

solder is 4.0%; the proportion of copper in the solder is 0.5%; and the proportion of phosphorous in the solder is 0.01%.

A further aspect of the present invention provides a method of soldering, comprising the step of using a substantially lead-free solder comprising: from 88.5% to 93.5% tin; from 3.5% to 4.5% silver; from 2.0% to 6.0% indium; and from 0.3% to 1.0% copper.

Preferably, the method comprises the step of using a solder comprising 91.3% tin, 4.2% silver, 4.0% indium and 0.5% copper.

Conveniently, the method comprises the step of using a solder comprising 91.39% tin, 4.1% silver, 4.0% indium, 0.5% copper and 0.01% phosphorous.

Advantageously, the method comprises the step of wave-soldering using the substantially lead-free solder.

In order that the present invention may be more readily understood, examples thereof will now be described, by way of example, with reference to the accompanying drawings, in which:

FIGURE 1 is a table of wetting times, in seconds, at a variety of temperatures, for a selection of different solders, including a solder embodying the invention;

FIGURE 2 is a graphical representation of the data expressed in the table of Figure 1;

FIGURE 4 is a graphical representation of the data expressed in the table of Figure 3;

FIGURE 5 is a table showing physical properties, including the coefficient of thermal expansion, of a selection of solders, including a solder embodying the present invention;

FIGURE 7 is a table of mechanical properties, including tensile strength and yield strength, for a selection of different solders, including a solder embodying the present invention;

FIGURE 9 is a table of results obtained in fillet lifting tests conducted on a selection of different lead-free solders, including a solder embodying the present invention;

FIGURE 10A and 10B are two pairs of micrograph images on two different scales, which pairs of images respectively show fillets of the solder embodying the invention adhering to nickel/gold and OSP coatings (polymer coatings on a copper substrate);

FIGURE 11 is a table showing the dissolution rate of copper into various types of solder, including a lead-free solder embodying the present invention;

FIGURE 12 is a graphical representation of the data expressed in the table of Figure 11; and

FIGURE 13 is a table showing the level of drossing exhibited by various solders, including a lead-free solder embodying the present invention.

As described above, conventional lead-free solders suffer from several drawbacks, including poor wetting properties, low fluidity, poor compatibility with existing component coatings, fillet lifting, high copper dissolution rates and excessive drossing when compared with conventional solders containing lead.

However, it has now been found that a solder embodying the present invention and composed of a lead-free alloy comprising from 88.5% to 93.2% tin, from 3.5% to 4.5% silver, from 2.0% to 6.0% indium, from 0.3% to 1.0% copper and up to 0.5% of an anti-oxidant or anti-skinning additive, such as phosphorous or another non-metallic compound or element, possesses significantly improved properties when compared with known lead-free solders. Indeed the properties of solders embodying the present invention are comparable to conventional solders containing lead as regards wettability, fluidity, compatibility with existing component coatings, fillet lifting, copper dissolution rate and drossing.

In order to demonstrate the advantageous properties of solders embodying the present invention, five tests were carried out, as will be

described below. These tests were carried out on a preferred embodiment of the solder of the present invention which is herein called ALLOY 349 and comprises 91.39% tin, 4.2% silver, 4.0% indium, 0.5% copper and 0.01% phosphorous.

Test 1: Wettability

The first test concerned the wettability of a sample of the solder embodying the present invention, as compared to samples of a selection of known solders, namely eight existing lead-free solders and a conventional lead-containing solder.

The nine known solders were as follows:

1. A lead-containing solder of the composition: 63% Sn; 37%Pb.
2. A first lead-free solder of the composition: 99.3%Sn; 0.7%Cu.
3. A second lead-free solder of the composition: 96.5%Sn; 3.5Ag.
4. A third lead-free solder (herein called VIROMET 217) of the composition: 88.3%Sn; 3.2%Ag; 4.5%Bi; 4.0%In.
5. A fourth lead-free solder (herein called VIROMET 411) of the composition: 92%Sn; 2%Cu; 3%Ag; 3%Bi.
6. A fifth lead-free solder (herein called VIROMET 513) of the composition: 92.8%Sn; 0.7%Cu; 0.5%Ga; 6%In.
7. A sixth lead-free solder of the composition: 93.5%Sn; 3.5%Ag; 3.0%Bi.
8. A seventh lead-free solder of the composition: 95.5%Sn; 4.0%Ag; 0.5%Cu.
9. An eighth lead-free solder of the composition: 96.0%Sn; 2.5%Ag; 1.0%Bi; 0.5%Cu.

1. The first part of the document is a list of names and their corresponding addresses. The names are: "John Doe", "Jane Smith", "Bob Johnson", "Alice Brown", "Charlie White", "David Green", "Eve Black", "Frank Gray", "Grace Hall", "Henry King", "Ivy Lee", "Jack Miller", "Karen Wilson", "Leo Young", "Mia Fox", "Noah Hill", "Olivia Scott", "Peter Adams", "Quinn Baker", "Samuel Carter", "Tina Evans", "Uma Friedman", "Victor Garcia", "Wendy Harris", "Xavier Jenkins", "Yara Khan", "Zoe Lewis". The addresses are: "123 Main St, New York, NY 10001", "456 Elm St, Los Angeles, CA 90001", "789 Oak St, Chicago, IL 60601", "101 Pine St, San Francisco, CA 94101", "202 Cedar St, Boston, MA 02101", "303 Birch St, Philadelphia, PA 19101", "404 Walnut St, Washington, DC 20001", "505 Spruce St, Houston, TX 77001", "606 Ash St, Phoenix, AZ 85001", "707 Hickory St, San Antonio, TX 78201", "808 Maple St, Dallas, TX 75201", "909 Poplar St, San Diego, CA 92101", "1010 Willow St, Austin, TX 78701", "1111 Sycamore St, Fort Worth, TX 76101", "1212 Dogwood St, Columbus, GA 31901", "1313 Magnolia St, Indianapolis, IN 46201", "1414 Redwood St, Jacksonville, FL 32201", "1515 Cypress St, Louisville, KY 40201", "1616 Juniper St, Memphis, TN 38101", "1717 Fir St, Milwaukee, WI 53201", "1818 Hemlock St, Nashville, TN 37201", "1919 Cypress St, New Orleans, LA 70112", "2020 Elm St, Portland, ME 04101", "2121 Oak St, Salt Lake City, UT 84101", "2222 Pine St, Sacramento, CA 95801", "2323 Birch St, Springfield, MA 01101", "2424 Walnut St, Tallahassee, FL 32301", "2525 Spruce St, Topeka, KS 66601", "2626 Ash St, Trenton, NJ 08601", "2727 Hickory St, Wichita, KS 67201", "2828 Maple St, Yonkers, NY 10461", "2929 Poplar St, Albany, NY 12201", "3030 Willow St, Binghamton, NY 13901", "3131 Sycamore St, Rochester, NY 14601", "3232 Dogwood St, Syracuse, NY 13201", "3333 Magnolia St, Utica, NY 13501", "3434 Redwood St, Oswego, NY 13127", "3535 Cypress St, Plattsburgh, NY 12169", "3636 Juniper St, Watkins Glen, NY 13854", "3737 Fir St, Cortlandt, NY 13820", "3838 Hemlock St, Oneonta, NY 13827", "3939 Cypress St, Canastota, NY 13312", "4040 Elm St, Amsterdam, NY 12006", "4141 Oak St, Schenectady, NY 12302", "4242 Pine St, Albany, NY 12201", "4343 Birch St, Troy, NY 12180", "4444 Walnut St, Rensselaer, NY 12150", "4545 Spruce St, Saratoga Springs, NY 12158", "4646 Ash St, Schenectady, NY 12302", "4747 Hickory St, Albany, NY 12201", "4848 Maple St, Troy, NY 12180", "4949 Poplar St, Rensselaer, NY 12150", "5050 Willow St, Saratoga Springs, NY 12158".

1. The first part of the document is a list of names and their corresponding addresses. The names are: "John Doe", "Jane Smith", "Bob Johnson", "Alice Brown", "Charlie White", "David Green", "Eve Black", "Frank Gray", "Grace Hall", "Henry King", "Ivy Lee", "Jack Miller", "Karen Wilson", "Leo Young", "Mia Fox", "Noah Hill", "Olivia Scott", "Peter Adams", "Quinn Baker", "Samuel Carter", "Tina Evans", "Uma Friedman", "Victor Garcia", "Wendy Harris", "Xavier Jenkins", "Yara Khan", "Zoe Lewis". The addresses are: "123 Main St, New York, NY 10001", "456 Elm St, Los Angeles, CA 90001", "789 Oak St, Chicago, IL 60601", "101 Pine St, San Francisco, CA 94101", "202 Cedar St, Boston, MA 02101", "303 Birch St, Philadelphia, PA 19101", "404 Spruce St, San Diego, CA 92101", "505 Willow St, Austin, TX 78701", "606 Hickory St, Portland, OR 97201", "707 Cypress St, Denver, CO 80201", "808 Redwood St, Seattle, WA 98101", "909 Sycamore St, Minneapolis, MN 55401", "1010 Dogwood St, St. Louis, MO 63101", "1111 Magnolia St, Nashville, TN 37201", "1212 Juniper St, Salt Lake City, UT 84101", "1313 Fir St, Anchorage, AK 99501", "1414 Hemlock St, Juneau, AK 99801", "1515 Larch St, Fairbanks, AK 99701", "1616 Alder St, Sitka, AK 99801", "1717 Basswood St, Kodiak, AK 99588", "1818 Cottonwood St, Wrangell, AK 99801", "1919 Elm St, Haines, AK 99824", "2020 Fir St, Haines Junction, AK 99824", "2121 Hemlock St, Haines, AK 99824", "2222 Juniper St, Haines, AK 99824", "2323 Larch St, Haines, AK 99824", "2424 Magnolia St, Haines, AK 99824", "2525 Redwood St, Haines, AK 99824", "2626 Sycamore St, Haines, AK 99824", "2727 Spruce St, Haines, AK 99824", "2828 Willow St, Haines, AK 99824", "2929 Birch St, Haines, AK 99824", "3030 Cedar St, Haines, AK 99824".

1. The first part of the document is a list of names and their corresponding addresses. The names are: "John Doe", "Jane Smith", "Bob Johnson", "Alice Brown", "Charlie White", "David Green", "Eve Black", "Frank Gray", "Grace Hall", "Henry King", "Ivy Lee", "Jack Miller", "Karen Wilson", "Leo Young", "Mia Fox", "Noah Hill", "Olivia Scott", "Peter Adams", "Quinn Baker", "Samuel Carter", "Tina Evans", "Uma Friedman", "Victor Garcia", "Wendy Harris", "Xavier Jenkins", "Yara Khan", "Zoe Lewis". The addresses are: "123 Main St, New York, NY 10001", "456 Elm St, Los Angeles, CA 90001", "789 Oak St, Chicago, IL 60601", "101 Pine St, San Francisco, CA 94101", "202 Cedar St, Boston, MA 02101", "303 Birch St, Philadelphia, PA 19101", "404 Spruce St, San Diego, CA 92101", "505 Willow St, Austin, TX 78701", "606 Hickory St, Portland, OR 97201", "707 Cypress St, Denver, CO 80201", "808 Redwood St, Seattle, WA 98101", "909 Sycamore St, Minneapolis, MN 55401", "1010 Dogwood St, St. Louis, MO 63101", "1111 Magnolia St, Nashville, TN 37201", "1212 Juniper St, Salt Lake City, UT 84101", "1313 Fir St, Anchorage, AK 99501", "1414 Hemlock St, Juneau, AK 99801", "1515 Larch St, Fairbanks, AK 99701", "1616 Alder St, Sitka, AK 99801", "1717 Basswood St, Kodiak, AK 99588", "1818 Cottonwood St, Wrangell, AK 99801", "1919 Elm St, Haines, AK 99824", "2020 Fir St, Haines Junction, AK 99824", "2121 Hemlock St, Haines, AK 99824", "2222 Juniper St, Haines, AK 99824", "2323 Larch St, Haines, AK 99824", "2424 Magnolia St, Haines, AK 99824", "2525 Redwood St, Haines, AK 99824", "2626 Sycamore St, Haines, AK 99824", "2727 Spruce St, Haines, AK 99824", "2828 Willow St, Haines, AK 99824", "2929 Birch St, Haines, AK 99824", "3030 Cedar St, Haines, AK 99824".

COPIES

solder embodying the present invention performed better overall in the first aspect of the first test than any of the existing lead-free solders.

The results of the first aspect of the first test are displayed in graphical form in Figure 2. It will be seen from this graph that the results representing the performances of the conventional solder containing lead and the solder embodying the present invention follow each other quite closely when compared to those representing the performances of the other lead-free solders.

A second aspect of the first test comprised the measurement of the maximum wetting force at 2.0 seconds after immersion of the specimen in the respective solders. The wetting force is, as described above, the adhesive force between the solder and the specimen. Clearly, the wetting force provides a useful indication of the strength with which a solder binds to a substrate, and a high wetting force is a desirable property for a solder.

The results of the second aspect of the first test are shown in Figure 3. To summarise these results, the solder embodying the present invention exhibited a maximum wetting force 2.0 seconds after immersion of the specimen therein, at each of the considered temperatures, that was comparable to that displayed by the conventional lead-containing solder, although somewhat lower. While some of the existing lead-free solders displayed a wetting force that was closer to that of the conventional leaded solder at some temperatures, only VIROMET 217 produced slightly better overall results and the solder of the present invention exhibited a wetting force that was close to that of the conventional lead-containing solder at all of the considered temperatures. This property of the solder embodying the present invention allows the solder of the invention to behave in a similar manner to conventional

lead-containing solders under a variety of temperature conditions, or where soldering takes place under varying temperature conditions.

The results of the second aspect of the first test are displayed in graphical form in Figure 4, which clearly shows that the results for the solder embodying the present invention follow those representing the conventional lead-containing solder at least as closely as the best of those representing the other lead-free solders.

From the results of the first test, it can be seen that the solder embodying the present invention exhibits very similar properties, with regard to wettability, to the conventional lead-containing solder. Clearly, this similarity in physical properties renders the solder embodying the present invention suitable for use as a replacement for the conventional lead-containing solder.

Test 2: Mechanical Properties

A second test compared the mechanical properties of the solder of the present invention with the mechanical properties of a conventional lead-containing solder. In this second test, various mechanical tests were carried out in accordance with the ASTM standard to compare the properties of ALLOY 349, the solder embodying the present invention, with a conventional lead-containing solder with the composition 63%Sn/37%Pb and seven other existing lead-free solders, with the following compositions:

1. A first lead-free solder: 99.3%Sn; 0.7%Cu.
2. A second lead-free solder: 96.5%Sn; 3.5Ag.
3. A third lead-free solder (herein called VIROMET 217): 88.3%Sn; 3.2%Ag; 4.5% Bi; 4.0% In.

4. A fourth lead-free solder (herein called VIROMET HF): 92.8 %Sn; 0.7%Cu; 0.5%Ga; 6%In.
5. A fifth lead-free solder: 93.5%Sn; 3.5%Ag; 3.0%Bi.
6. A sixth lead-free solder: 95.5%Sn; 4.0%Ag; 0.5%Cu.
7. A seventh lead-free solder: 96%Sn; 2.5%Ag; 0.5%Cu; 1.0%Bi.

A first aspect of this second test involved determining the melting temperature, the coefficient of thermal expansion (CTE) and the specific gravity (SG) of the solders under test. The results of this first aspect of the second test are tabulated in Figure 5 and illustrated in graphical form in Figure 6.

As will be appreciated from the table and graph, the ALLOY 349 solder of the present invention proved to have a thermal expansion co-efficient which is very close to the conventional lead-containing solder, so that any fear of incompatibility between the invention and existing components and boards is significantly reduced.

A second aspect of the second test involved measuring the tensile strength, load at maximum load, yield strength and Young's Modulus of the various solders. The results of these tests are expressed in full in the table of Figure 7, while Figure 8 graphically shows the tensile strength and yield strength of each of the alloys.

As will be seen from Figures 7 and 8, the results of this test demonstrate that the ALLOY 349 solder embodying the present invention has a better strength and better Young's Modulus compared to the conventional lead-containing solder, thereby indicating that fillet joints made of the alloy in

accordance with the invention can potentially be much stronger than joints made from the conventional lead-containing solder.

Test 3: Fillet Lifting

The increasing use of lead-free solders in the various industries has shown that there is a tendency for fillet lifting to occur when lead-free solders are used in the context of printed circuit boards with through-plated holes employing both OSP and Ni/Au coatings.

In a third test, the occurrence of such fillet lifting was tested for a selection of lead-free solders, namely the ALLOY 349 solder embodying the present invention and the following six existing lead-free solders:

1. A first lead-free solder: VIROMET 217.
2. A second lead-free solder: 92.3%Sn; 3.2%Ag; 0.5%Bi; 4.0%. 12
3. A third lead-free solder: 89.8%Sn; 3.2%Ag; 1.0%Bi; 6.0%In.
4. A fourth lead-free solder: 88.8%Sn; 3.2%Ag; 2.0%Bi; 6.0%In.
5. A fifth lead-free solder: 94.5%Sn; 4.0%Ag; 0.5% Cu; 1.0% Bi.
6. A sixth lead-free solder: 96.5%Sn; 3.5%Ag.

The results of this third test are illustrated in Figures 9, 10A and 10B, Figure 9 showing the results in tabulated form. Figures 10A and 10B show micrographs, on two different scales, of fillet joints formed using the ALLOY 349 solder embodying the present invention on Ni/Au and OSP coatings, respectively. These results clearly indicate that the use of a solder embodying the present invention enables the elimination of fillet lifting defects in the context of OSP and nickel/gold coated through-holes in printed circuit boards.

Test 4: Copper Dissolution Rate

A fourth test was carried out to compare the copper dissolution rate in a lead-free solder embodying the present invention with a conventional lead-containing solder (63%Sn/37%Pb) and three existing lead-free solders as follows;

1. A first lead-free solder: VIROMET 217.
2. A second lead-free solder: 99.3%Sn; 0.7%Cu.
3. A third lead-free solder: 95.5%Sn; 4.0%Ag; 0.5%Cu.

The testing was carried out by dipping a known weight of fluxed copper plate into the melted solder and the concentration of the copper in the solder was subsequently measured using inductively coupled plasma equipment. The rate of copper dissolution was then calculated on the basis of the concentration of the copper found in the solder against the weight of copper dipped in the solder.

The results of this fourth test are expressed in Figures 11 and 12, which respectively show the results in tabulated form and in graphical form. As will be seen from Figures 11 and 12, the alloy embodying the present invention has a slightly higher rate of copper dissolution than the conventional lead-containing solder but also has one of the lowest copper dissolution rates found in the lead-free solders tested.

Test 5: Drossing

A fifth test was concerned with the suitability of the solder of the present invention for use in a wave-soldering machine. In an example of wave-soldering, a circuit board is held just above the surface of a quantity of molten

When using existing lead-free solders, the levels of dross present in the pot after several uses have been found in some cases to be unacceptably high.

1. A first lead-free solder: VIROMET 217.
2. A second lead-free solder: 99.3%Sn; 0.7%Cu.
3. A third lead-free solder: 95.5%Sn; 4.0%Ag; 0.5%Cu.

In this test, the solder being tested was used in a pot of molten solder in a simulated conventional wave-soldering machine. No alteration of the machine was made to accommodate the use of the solder and the wave-soldering machine was used to solder circuit boards in the same way as for a conventional tin/lead solder. The wave-soldering machine was operated in a normal air environment at a pot temperature of 245° C, with the boards being conveyed over the surface of the pot at a speed of 1.4 to 1.8m/min. At the end of each of four successive 15 minute periods of operation, the dross in the pot was removed and weighed to determine the amount of dross produced by the wave-soldering process in each period. The weights were then totalled to give a measurement of the rate of dross production per hour. The results of this fifth

test are tabulated in Figure 13 which demonstrates clearly that the solder embodying the present invention produces dressing to a degree which is lower than all but one of the other lead-free solders and is lower than the dressing found with the conventional lead-containing solder.

As will be appreciated from the above results, the present invention provides a lead-free solder that is very suitable for use as a direct replacement for conventional lead-containing solders, due to the comparable characteristics of wettability, fluidity, compatibility with existing component coatings, fillet lifting and dressing exhibited by the solder of the present invention.

Consequently, the need for manufacturers to replace existing machinery, processes or component coatings to accommodate use of a lead-free solder can be eliminated or substantially reduced by employing a solder embodying the present invention. As a result, the process of converting a manufacturer's facility to the use of lead-free solder may be rendered far simpler and more economically viable than hitherto contemplated.

In the present specification "comprises" means "includes or consists of" and "comprising" means "including or consisting of".

The features disclosed in the foregoing description, or the following claims, or the accompanying drawings, expressed in their specific forms or in terms of a means for performing the disclosed function, or a method or process for attaining the disclosed result, as appropriate, may, separately, or in any combination of such features, be utilised for realising the invention in diverse forms thereof.